## 1,1,3,3-Tetramethylguanidne Solvated Lanthanide Aryloxides: Pre-catalysts for

## Intramolecular Hydroalkoxylation

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**Fig. S2.** Thermal ellipsoid plot of **4**. Ellipsoids are drawn at the 30 % level. H atoms have been omitted for clarity.

**Fig. S3.** Thermal ellipsoid plot of **6**. Ellipsoids are drawn at the 30 % level. H atoms have been omitted for clarity.

**Fig. S4.** Thermal ellipsoid plot of **7**. Ellipsoids are drawn at the 30 % level. H atoms have been omitted for clarity.

**Fig. S5.** Thermal ellipsoid plot of **8**. Ellipsoids are drawn at the 30 % level. H atoms have been omitted for clarity.

**Fig. S6.** <sup>1</sup>H NMR spectra (400 MHz,  $C_6D_6$ ) showing the progress of a cycloisomerization reaction catalyzed by La(DBP)<sub>2</sub>(HTMG)<sub>2</sub>(O(CH<sub>2</sub>)<sub>3</sub>C=CH).

**Fig. S7.** Variable temperature <sup>1</sup>H NMR ( $C_6D_6$ ) of 7 taken at 10 °C increments from 25 °C to 65 °C.

**Fig. S1.** Thermal ellipsoid plot of **2**. Ellipsoids are drawn at the 30 % level. H atoms have been omitted for clarity. Selected inter-atomic distances (Å) and angles (°) for **S1**: La(1)-O(3) 2.132(3), La(1)-N(1) 2.620(4), La(1)-O(1) 2.309(3), La(1)-O(2) 2.326(3), La(1)-N(4) 2.626(4), O(3)-La(1)-O(1) 104.86(11), O(1)-La(1)-O(2) 149.33(10), O(3)-La(1)-N(1) 102.86(13), O(1)-La(1)-N(1) 76.35(11), O(2)-La(1)-N(1) 98.02(11), N(1)-La(1)-N(4) 158.27(13), C(29)-N(1)-La(1) 152.5(3), La(1)-N(1)-H(1) 103.7, C(34)-N(4)-La(1) 152.0(3), La(1)-N(4)-H(4) 104.0, C(4)-O(1)-La(1) 168.9(2).



**Fig. S2.** Thermal ellipsoid plot of **4**. Ellipsoids are drawn at the 30 % level. H atoms have been omitted for clarity. Selected inter-atomic distances (Å) and angles (°) for **S2**: La(1)-O(3) 2.149(8), La(1)-O(2) 2.304(6), La(1)-O(1) 2.327(6), La(1)-N(1) 2.621(8), La(1)-N(4) 2.605(9), O(3)-La(1)-O(2) 108.9(3), O(2)-La(1)-O(1) 139.5(2), O(3)-La(1)-N(4) 96.3(3), O(1)-La(1)-N(4) 80.9(3), N(4)-La(1)-N(1) 159.0(3), C(4)-O(1)-La(1) 172.9(6), C(34)-N(1)-La(1) 146.9(7).



**Fig. S3**. Thermal ellipsoid plot of **6**. Ellipsoids are drawn at the 30 % level. H atoms have been omitted for clarity. Selected inter-atomic distances (Å) and angles (°) for **S3**: La(1)-O(2) 2.225(4), La(1)-O(1) 2.251(3), La(1)-O(3) 2.265(3), La(1)-N(1A) 2.462(11), La(1)-N(1) 2.507(9), O(2)-La(1)-O(1) 110.70(14), O(2)-La(1)-O(3) 117.79(14), O(2)-La(1)-N(1A) 99.8(3), O(3)-La(1)-N(1) 81.8(2), N(1A)-La(1)-N(1) 26.4(3), C(43)-N(1)-La(1) 142.5(8), C(1)-O(1)-La(1) 155.3(4).





**Fig. S4.** Thermal ellipsoid plot of **7**. Ellipsoids are drawn at the 30 % level. H atoms have been omitted for clarity.

Fig. S5. Thermal ellipsoid plot of 8. Ellipsoids are drawn at the 30 % level. H atoms have been omitted for clarity.



**Fig. S6.** <sup>1</sup>H NMR spectra (400 MHz,  $C_6D_6$ ) showing the progress of a cycloisomerization reaction catalyzed by **4**. Ph<sub>3</sub>SiCH<sub>3</sub> is also included as an internal integration standard. The initial spectrum (A) was obtained just as the reaction mixture was allowed to warm to room temperature and specific staring material peaks are labeled. Spectrum B was obtained after maintaining the reaction temperature at 60 °C for 11 hours. Spectrum C was obtained after a total of 22 hours at 60 °C. The staring material has been consumed and specific product peaks are labeled.



**Fig. S7.** Variable temperature <sup>1</sup>H NMR ( $C_6D_6$ ) of 7 taken at 10 °C increments from 25 °C to 65 °C.

